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# Long Term Isothermal Aging and Thermal Analysis of N-CYCAP Polyimides

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## N-CYCAP POLYIMIDES

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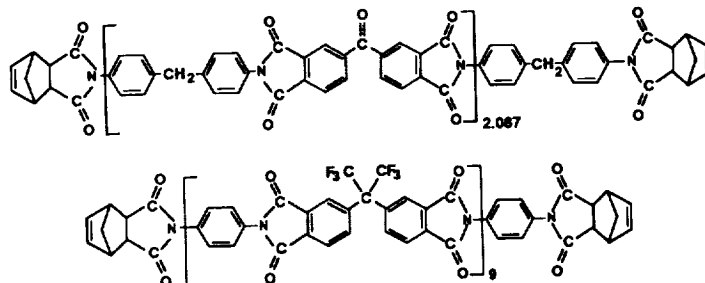
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### SUMMARY

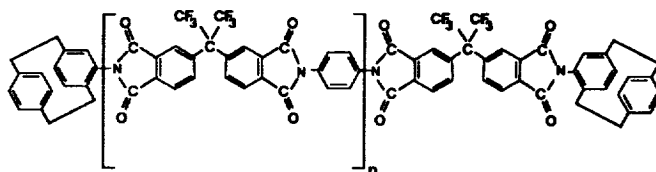
N-CYCAP polyimides utilize a [2.2] paracyclophane endcap that polymerizes and does not generate volatile gases during the cure process. These polyimides have both high glass transition temperatures (390 °C) and an onset of decomposition in air of 560 °C. Thermal oxidative stability (TOS) weight loss studies show that replacing 25 percent by weight of the paraphenylene diamine in the polymer backbone with meta-phenylene diamine improves the weight loss characteristics. N-CYCAP neat resin samples performed better than PMR-II-50 when exposed at 343 and 371 °C in air for up to 1000 hr. Preliminary composite studies show that both PMR-II-50 and N-CYCAP have better thermal stability when fabricated on T-40R. Higher isothermal aging temperatures of longer aging times are needed to determine the differences in TOS between composite samples of PMR-II-50 and N-CYCAP polyimides.

### INTRODUCTION

A major research goal at the NASA Lewis Research Center is the development of new polymer matrix resins for high temperature applications. A prominent resin used to replace metallic components in aircraft engines where temperatures can reach 300 °C is PMR-15 (structure 1). Another resin being considered for even higher temperature environments is PMR-II-50 (structure 2). Both of these polymers contain the nadic carboxylic acid ester as a monomer in an addition curing polyimide. Vannucci and Malarik (ref. 1) have demonstrated that the nadic endcap is the weak link in both of these addition curing polyimides.



One objective when developing high temperature resins is to replace the nadic acid ester endcap with an endcap that is more thermally stable. These new resins should maintain similar processing conditions to those of PMR-15 and PMR-II-50 when formulated to similar molecular weights. One newly developed resin system contains a paracyclophane imidized endcap, termed N-CYCAP (amine substituted CYClophane Addition Polyimides). The resin system formulated from 4-amino[2.2]paracyclophane contains a strained ring system as the site of addition crosslinking. N-CYCAP polyimides contain fewer carbon-carbon single bonds, have increased aromatic ring content, and emit no volatiles during the cure cycle (ref. 2).



## EXPERIMENTAL

All monomers and solvents were used as-received. All thermal analyses were recorded on either an Omnitherm 35050 Thermal Analysis System or an Omnitherm Advantage II Thermal Analysis System at a scan rate of 10 °C/min. Thermomechanical analyses were carried out with a DuPont Instruments 943 TMA on postcured neat resin disks. Differential scanning calorimetry was carried out on imidized molding powders in a DuPont Instruments DSC cell under ambient air.

Compression molding (1000 psi) was performed in a circular hardened steel die with brass plungers. The charged die was placed in a press preheated to the process temperature, and the ramp rate of the die was approximately 20 °C/min. All polymerized specimens were cooled to room temperature under pressure. Isothermal weight loss studies were conducted in triplicate on neat resin samples, all cut to the same size (5.1 mm x 5.1 mm x 1.8 mm), at 343 and 371 °C in a forced hot air oven under 1 atmosphere flowing air.

Prepregs were prepared by filament winding the respective fibers and by applying approximately a 50 percent by weight solution of monomers in chloroform. Laminates were processed using a simulated autoclave technique at 200 psi as in Vannucci et al. (ref. 1).

## RESULTS AND DISCUSSION

N-CYCAP polyimides were formulated from a variety of aromatic diamines and dianhydrides. Some of the most thermal stable resins were formulated from 4-amino[2.2] paracyclophane, hexafluoro dianhydride (HFDA), paraphenylene diamine (p-PDA), and metaphenylene diamine (m-PDA). Samples of molding powders from these monomers were compression molded at 316, 343, 371, and 398 °C. The cure cycle of these polyimides was identical to that of the corresponding PMR-II powders with similar molecular weights. Typically, the N-CYCAP polyimides were compression molded into void-free neat resins on the first attempt.

The cyclophane endcapped polyimides polymerize vigorously and their exotherms were studied for samples with formulated molecular weights (FMW) of 1886 and 6030 (fig. 1). These molding powders correspond to polyimides with  $n$  values of 2 and 10 where the weight percent of the cyclophane endcap is 24 and 7.5, respectively. The differential scanning calorimetry (DSC) experiments showed two exotherms for all N-CYCAP polyimides. The temperatures at which these exotherms began to occur were 250 and 350 °C.

[2.2] Cyclophane containing polymers were studied previously (ref. 3). The bond cleavage in N-CYCAP polyimides during curing of the resins leads to crosslinked polymers with high glass transition temperatures and excellent thermal oxidative stability. The glass transition temperatures ( $T_g$ ) of air-postcured (16h) N-CYCAP polyimides were reported previously to be as high as 353 °C (ref. 2). The effect of a nitrogen postcure was examined for N-CYCAP polyimides. The highest  $T_g$  obtained after nitrogen postcuring was 390 °C (table I).

Thermal oxidative weight loss studies (TOS) compared the neat resin stabilities of N-CYCAP to PMR-II-50 (fig. 2 and table II). The neat resins were aged at 343 and 371 °C in air. The effects of postcuring in different environments were also studied to determine the stabilities of the neat resins postcured in air versus nitrogen (ref. 4). All neat resins were aged at 343 °C for 1000 hr. Resins aged at 371 °C for 600 hr or more decomposed and could not be weighed accurately.

The TOS study performed at 343 °C clearly demonstrates the excellent stability of N-CYCAP resins containing metaphenylene diamine (m-PDA) (fig. 2). The sample containing 25-percent m-PDA lost only 10.5 percent of the resins total weight after 1000 hr. This neat resin specimen performed better than any other sample in both the 343 and 371 °C aging studies. The best PMR-II sample lost 14.6 percent of its weight after the same period of time. This ranking was also observed when the resins were nitrogen postcured before the 343 °C aging study began (fig. 2). The N-CYCAP sample containing 25-percent m-PDA that was nitrogen postcured at 371 °C and aged at 343 °C in air lost 24.2 percent of its weight while the best PMR-II sample lost 28.5 percent.

Weight loss studies at 371 °C follow a similar trend to the studies at 343 °C. Because of a rapid degradation of all resins tested at 371 °C, the best weight comparison can be seen after aging for 250 hr. After 250 hr the resins cracked and deteriorated quickly. The N-CYCAP resin containing 25-percent m-PDA lost only 7.4 percent of its weight while the best PMR-II sample lost 19.5 percent. The comparison of the best N-CYCAP resin (with 25-percent m-PDA) and the best PMR-II sample after 500 hr of aging at 371 °C in air follows the trend observed after 250 hr of aging. Wherein N-CYCAP lost 19.4 percent of its weight, the PMR-II-50 resin lost 37.9 percent of its weight after 500 hr.

Preliminary studies were performed to determine the long-term thermal stability and initial mechanical property of N-CYCAP and PMR-II-50 matrix resins on two types of graphite fiber composites. The results of these studies are shown in tables III and IV. The 343 °C isothermal aging study shows that the N-CYCAP and PMR-II-50 composites were comparable. All composites made from T-40R fiber were more stable than those fabricated from T650-42 fiber. The isothermal test temperature appears to have not been high enough to determine significant differences in the thermal stability of N-CYCAP and PMR-II-50 resins. The composites were tested for flexural and interlaminar shear strength (ILSS) and are shown in table IV. The N-CYCAP

composites performed better than the PMR-II-50 composites in the ILSS test at 343 °C whereas the PMR-II-50 composites performed better in the 343 °C flexural tests.

#### CONCLUSIONS

Resins and composites fabricated from N-CYCAP and PMR-II-50 were tested for their long-term thermal stability. N-CYCAP neat resins containing metaphenylene diamine and paraphenylene diamine performed better than the PMR-II-50 neat resins in the 343 and 371 °C TOS studies. N-CYCAP exhibited high T<sub>g</sub>'s (390 °C). Composite studies show that both N-CYCAP and PMR-II-50 have better thermal stability when fabricated on T-40R graphite fiber. Higher isothermal aging temperatures of longer aging times are needed to determine differences in these resin systems.

#### REFERENCES

1. Vannucci, R.D.; and Malarik, D.C.: Autoclave Cured Composites for 371 °C (700 °F) Applications. HiTEMP Review 1989, NASA CP-10039, 1989, pp. 15-1 to 15-8.
2. Sutter, J.K.; and Waters, J.W.: Long Term Isothermal Aging and Thermal Analysis of N-CYCAP Polyimides. HiTEMP Review 1990, NASA CP-10051, 1990, pp. 4-1 to 4-9.
3. (a) Meyers, R.A.; Hamersma, J.W.; and Green, H.E.: Paracyclophane Units: Versatile Segments for Polymer Chain Crosslink formation. Polymer Letters, Vol. 10, 1972, pp. 685-689. (b) Chang, D.M.; and Marvel, C.S.: Aromatic Polyethers, Polysulfones, and Polyketones as Laminating Resins. VII. Polymers with [2.2]-p-Cyclophane units. J. Polym. Sci Polym. Chem., Ed., Vol. 13, 1975, pp. 2507-2515. (c) Upshaw, T.A.; and Stille, J.K: [2.2] Paracyclophane End-Capped Polyquinoline Prepolymers: Synthesis, Processing, and Thermal Properties. Polym, Mater. Sci. Eng. Proc., vol. 59, 1988 pp. 553-557.
4. Bowles, K.J.: Thermo-Oxidative Stability Studies of PMR-15 Polymer Matrix Composites Reinforced with Various Continuous Fibers. SAMPE Proc. Vol. 35, Book 1, G. Janicki, V. Bailey, and H. Schjelderup, eds.,) 1988, pp. 147-161.

TABLE I. - RESIN GLASS TRANSITION TEMPERATURES

Resin <sup>a</sup>	No postcure	Postcure in air at 370 °C	Postcure in nitrogen at 371 °C	Postcure in nitrogen at 400 °C
	Glass transition temperature, °C			
PMR-II-50	301	365	387	408
N-CYCAP, n = 6	267	339	336	390
N-CYCAP, n = 10	323	353	357	382
N-CYCAP, n = 10 with 25 percent m-PDA	319	350	342	365

<sup>a</sup>All resins were cured for 2 hr at 371 °C.

TABLE II. - RESIN THERMAL OXIDATIVE WEIGHT LOSS STUDIES

Resin <sup>a</sup>	Postcure environment	Aging time, hr	
		250	500
		Weight loss, percent	
PRM-II-50	Air	19.5	37.9
	Nitrogen	16.8	32.5
N-CYCAP, n = 10 (100 percent p-PDA)	Air	13.2	30.0
	Nitrogen	14.4	30.2
N-CYCAP, n = 10 25 percent m-PDA	Air	7.4	19.4
	Nitrogen	10.7	21.7

<sup>a</sup>All resins were tested in 1 atm air; postcure temperature, 371 °C.

TABLE III. - 1000 HR ISOTHERMAL AGING at 343 °C

Resin	Composite weight loss, percent	
	T40R fiber	T650-42 fiber
N-CYCAP	5.8±0.9	6.5±0.5
N-CYCAP, 25 percent m-PDA	3.8±0.6	7.2±0.2
PMR-II-50	3.3±1.3	6.7±1.3
PRM-II-50, 25 percent m-PDA	3.4±0.4	7.6±1.6

TABLE IV. - FLEX STRENGTH and ILSS of COMPOSITES TESTED at 343 °C

Resin <sup>a</sup>	Fiber	Flex strength, ksi	ILSS, ksi	T <sub>g</sub> , °C
N-CYCAP	T40R	59.3±3.0	4.48±0.2	376
	T650-42	47.3±2.0	5.35±0.1	338
N-CYCAP, 25 percent m-PDA	T40R	46.5±2.1		360
	T650-42	35.8±1.4	5.11±0.5	330
PMR-II-50	T40R	69.6±4.1	3.50±0.18	386
	T650-42	81.2±2.6	4.09±0.12	372
PMR-II-50, 25 percent m-PDA	T40R	87.7±7.9	4.62±0.11	351
	T650-42	75.4±2.1	4.67±0.67	385

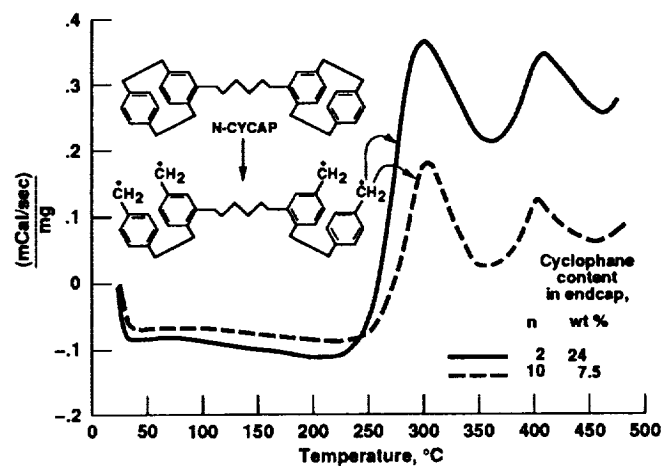


Figure 1.—DSC of N-CYCAP polyimides.

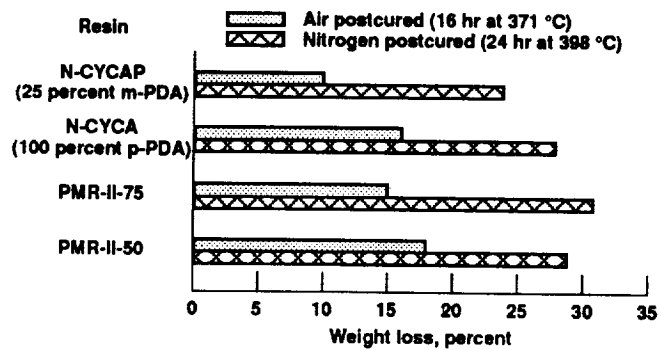


Figure 2.—Resin TOS after 1000 hours at 343 °C.





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